Application of Symmetry Correlations to Homogeneous Chemiluminescent Electron Transfer Reactions

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(Z. Naturforsch. **29 b**, 451–452 [1974]; received February 25, 1974)

Chemiluminescent redox reactions, Symmetry correlations

Light emission accompanying homogeneous electron transfer reactions between electrochemically produced anionic and cationic radicals of aromatic hydrocarbons in nonaqeous solvents (reaction (1)) has been the subject of numerous investigations in recent years. Interest in this area began with three reports[1] in which HERCULES and CHANDROSS *et al.* independently observed light emission in the vicinity of solid electrodes upon alternating current electrolysis of aromatic hydrocarbons.

$$R + e^- \rightarrow R^- \quad (1a)$$
$$R - e^- \rightarrow R^+ \quad (1b)$$
$$R^- + R^+ \rightarrow R + R^* \quad (1c)$$
$$R^* \rightarrow R + h\nu \quad (1d)$$

The proposed mechanism for this type of reaction was the initial transfer of an electron from the singly occupied antibonding molecular orbital of the anion to the unoccupied antibonding molecular orbital of the cation, followed by an intramolecular radiative emission from the excited hydrocarbon thus produced. MARCUS[2] treated the electrochemiluminescence phenomenon theoretically, using his general equation for electron transfer reactions and concluded that the emittive pathway was a reasonable one for the removal of excess energy in these exothermic reactions. Some examples of this type of redox reactions have been presented and reviewed[3] and work on the properties of these and new systems is continuing. For example, in a recent study[4] it was observed that the reactions involving dianions and dications of the same systems (reactions (2) and (3) are also capable of producing excited states, provided that the dianion or dication is sufficiently stable during the experiment. In reaction (2c) (similar to the

$$R + 2e^- \rightarrow R^= \quad (2a)$$
$$R - e^- \rightarrow R^+ \quad (2b)$$
$$R^= + R^+ \rightarrow R^- + R^* \quad (2c)$$
$$R^* \rightarrow R + h\nu \quad (2d)$$

$$R + e^- \rightarrow R^- \quad (3a)$$
$$R - 2e^- \rightarrow R^{++} \quad (3b)$$
$$R^- + R^{++} \rightarrow R^+ + R^* \quad (3c)$$
$$R^* \rightarrow R + h\nu \quad (3d)$$

case in reaction (1c)) the electron transfer occurs from the doubly occupied antibonding molecular orbital of the dianion to the unoccupied molecular orbital of the cation, whereas in reaction (3c) the electron transfer must be from the highest occupied bonding molecular orbital of the anion to the unoccupied bonding orbital of the dication (Fig. 1).

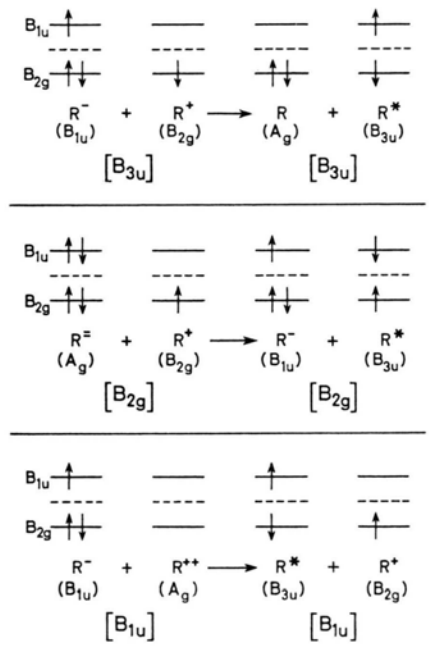

Fig. 1. Molecular orbitals and symmetry representations of the emittive pathways in electron transfer reactions of aromatic hydrocarbon radical ions of anthracene.

The importance of symmetry considerations in predicting the route and the nature of the products of some concerted chemical reactions[5] has attracted considerable attention among chemists. In those reactions to which the group theoretical correlations are applied, some chemical bonds are broken and some new bonds are formed. In spite of such complexities, the symmetry rules have successfully predicted the fate of these reactions. In electron transfer reactions of the type discussed above, no bonds are broken and no new bonds are formed. It should therefore be expected that symmetry rules can be more easily applied to these simple cases.

If we represent the wave function of the reactants as Ψ_R and that of the products as Ψ_P, these two must belong to the same irreducible representation of the point group of the molecule in order for a certain reaction to occur. The physical meaning of this is that the two wave functions must overlap in a nonvanishing manner. Let us now analyze reactions (1c, 2c and 3c) for a typical electrochemi-

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luminescent system such as anthracene. This molecule belongs to D_{2h} point group. The symmetry representations of all the species involved in the electron transfer reactions are given in Fig. 1. For reaction (1c), Ψ_R has a symmetry of $B_{1u} \times B_{2g} = B_{3u}$ and Ψ_P has a symmetry of $A_g \times B_{3u} = B_{3u}$, so that the initial and the final wave functions belong to the same irreducible representation of this point group. Therefore, the production of one of the neutral molecules in an excited state is an allowed process both thermodynamically and by symmetry. The production of both the molecules in the ground state ($R^+ + R^- \rightarrow R + R$) (which is also thermodynamically allowed process) would be symmetry forbidden. In the latter case the product wave function has $A_g \times A_g = A_g$ symmetry which does not match up with B_{3u} symmetry of the wave function of the reactants. This nonemittive pathway should not have a significant probability in the overall reaction mechanism. When the same simple procedure is carried out for reactions (2c and 3c), it is seen (Fig. 1) that for these processes also, the only symmetry allowed route is the one which generates a neutral molecule in an excited state.

Chemiluminescent anion–cation annihilation reactions of the above type; simple electron exchange reactions of type

$$R^- + R \rightarrow R + R^- \quad (4a)$$
$$R^+ + R \rightarrow R + R^+ \quad (4b)$$

and certain disproportionation or reproportionation reactions of type

$$R^- + R^- \rightarrow R + R^= \quad (5a)$$
$$R^+ + R^+ \rightarrow R + R^{++} \quad (5b)$$

$$R + R^= \rightarrow R^- + R^- \quad (6a)$$
$$R + R^{++} \rightarrow R^+ + R^+ \quad (6b)$$

are all known to be extremely fast bimolecular reactions whose rate constants[3b,6] are of the order of $\sim 10^6$–10^9 $l \cdot mole^{-1}$. Such large rate constants in all these cases, as well as the production of excited species in reactions (1c, 2c and 3c), are the natural consequence of the conservation of symmetry.

The financial support of the Alexander von Humboldt Foundation is gratefully acknowledged. The author wishes to thank Professor B. SCHRADER and the members of the Theoretical Organic Chemistry Department of the Dortmund University for valuable discussions.

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